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Synthesis and Thermal Cyclization Reactions of Methyl Isocrotonate Derivatives

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Methyl isocrotonate derivatives prepared from various 1,2-ethylenediamines, *o*-phenylenediamines, 2-aminoethanols or *o*-aminophenols with dimethyl acetylenedicarboxylate were easily converted to pyrido[1,2-*a*]pyrazines, pyrido[1,2-*a*]quinoxalines, pyrido[2,1-*c*]-1,4-oxazines, pyrido[2,1-*c*]-1,4-benzoxazines, respectively, and other cyclization compounds by means of thermal reactions.

Keywords—cyclization; thermal reaction; methyl isocrotonate derivative; X-ray analysis; pyrido[1,2-*a*]pyrazine; pyrido[1,2-*a*]quinoxaline; pyrido[2,1-*c*]-1,4-oxazine; pyrido[2,1-*c*]-1,4-benzoxazine; dimethyl acetylenedicarboxylate

Acetylenic esters are widely used for the preparation of heterocyclic compounds.¹⁾ As a part of our studies on the synthesis of heterocyclic compounds, we recently reported the results of the reactions of benzoxazoles²⁾ or nucleic acid bases³⁾ with dimethyl acetylenedicarboxylate (DMAD). Furthermore, we described a novel synthesis of pyrido[1,2-*a*]quinoxalines, pyrido[1,2-*a*]pyrazines, pyrido[2,1-*c*]-1,4-oxazine, pyrido[2,1-*c*]-1,4-benzoxazines and others.⁴⁾ Herein, we present additional information and complete experimental details of our work.

The reaction of *o*-phenylenediamine (**1**) with DMAD in MeOH at room temperature is known to produce 3-methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (**2a**).⁵⁾ The further reaction of **2a** with DMAD under reflux in dioxane overnight afforded methyl 3-oxo-1,2,3,4-tetrahydroquinoxaline- β,γ -bismethoxycarbonyl- $\Delta^{2,\gamma}$ -isocrotonate (**3a**).^{4a)} This compound (**3a**) could also be obtained directly by the reaction of *o*-phenylenediamine (**1a**) with DMAD in refluxing dioxane overnight^{4a)} as shown in Chart 1. The structure of **3a** was supported by the satisfactory elemental analysis and by comparing its spectral data with those of a similar compound, methyl 2,3-dihydro-2-oxo-4*H*-1,4-benzoxazine- β,γ -bismethoxycarbonyl- $\Delta^{2,\gamma}$ -isocrotonate (**3b**, $R_1 = R_2 = H$).²⁾ Other compounds (**3b**, **6a** and **6b**) were also prepared in a similar manner. We have subsequently investigated the thermal reaction of these methyl isocrotonate derivatives.

A solution of **3a** ($R_1 = R_2 = H$) in dry dimethyl sulfoxide (DMSO) was refluxed for 1 h

Chart 2

Chart 3

$\text{C}_{17}\text{H}_{14}\text{ClNO}_7$ which showed that this product is a deoxygenated compound of the starting material (**3b**, $\text{C}_{17}\text{H}_{14}\text{ClNO}_8$). The ^1H -NMR spectrum of this compound (**9**) showed the presence of three methyl esters at δ 3.60, 3.68 and 3.70, three aromatic protons at δ 6.89–7.51 and an amino proton at δ 10.09. A vinyl proton signal at δ 6.95 (1H, s) observed in **3b** ($R_1 = \text{H}$, $R_2 = \text{Cl}$) disappeared and instead, a signal at δ 4.47 (1H, s) appeared. The ^{13}C -NMR spectrum showed a signal at δ 49.60 which became a doublet in the single frequency off-resonance mode. These new signals (δ 4.47 and 49.60) suggested the presence of a methine carbon having a methoxycarbonyl group. Moreover, the infrared (IR) spectrum of **9** lacked the absorption at 1769cm^{-1} observed in the case of **3b** ($R_1 = \text{H}$, $R_2 = \text{Cl}$), indicating the absence of a lactone structure in the molecule. From the data described above, this compound was considered to have a novel tricyclic structure, trimethyl 2,3-cyclopenta-1',3'-dieno-6-chloro-1,4-

benzoxazine-3',4',5'-tricarboxylate (**9'**).^{4b)} In order to confirm the structure of this compound, we carried out an X-ray crystallographic analysis and the structure was revised as shown in Chart 3. In Fig. 1, the correct structure of **9** is shown: trimethyl 2,3-cyclopenta-1'(4'),2'-dieno-6-chloro-1,4-benzoxazine-3',4',5'-tricarboxylate (**9**). The atomic parameters of **9** obtained are listed in Table I, and the bond lengths and bond angles are shown in Table II. The formation of **9** can be formulated as the result of an electrocyclic reaction accompanying a deoxygenation process as shown in Chart 4.

Chart 4

A small amount (3.4% yield) of a second product was also obtained from the pyrolysis mixture as colorless fine prisms [**10**, mp 178°C, MS m/z 305 and 307 ($M^+/2$)]. The novel structure of this compound was unequivocally determined by a crystallographic study. In Fig. 2, the molecular structure of **10** and the atomic numbering system are shown. The atomic parameters, bond lengths and bond angles are given in Tables III and IV. The mechanism of the formation of this dimerization product (**10**) was not clear but a compound assumed to be an intermediate in the formation of **10** was formed in the next pyrolysis.

Another pyrolysis of **3b** ($R_1 = \text{H}$, $R_2 = \text{Cl}$) was carried out in the same manner but for a shorter time than in the case of the previous pyrolysis. In addition to the starting material (**3b**) and **9** (17.3% yield), two new crystalline compounds were obtained. The first product (**11**, 11.9% yield) has the empirical formula $\text{C}_{16}\text{H}_{10}\text{ClNO}_7$, which indicated that this compound was prepared by elimination of MeOH from **3b**. The $^1\text{H-NMR}$ spectrum of **11** showed the presence of two methyl esters at δ 3.95 and 4.00, two aromatic protons at δ 7.19—7.46, a vinyl proton at δ 7.61 (s) and a downfield-shifted aromatic proton at δ 9.28 (d, $J = 2.2$ Hz). In contrast to the result of the pyrolysis of **3a**, the structure of **11** was assigned to be dimethyl 2-chloro-6,10-dioxypyrido[2,1-*c*]-1,4-benzoxazine-7,8-dicarboxylate.

The $^1\text{H-NMR}$ spectrum of the second product (**12**, 4.1% yield) showed the presence of two vinyl protons at δ 7.59 (d) and δ 8.01 (d) which are coupled to each other with a J value of 1.95 Hz. This value is presumed to be a *meta*-coupling value. Moreover, one aromatic proton signal (δ 9.51) resonates at a very low magnetic field. From these data, this compound (**12**) was considered to be a demethoxycarbonyl derivative of **9**, and hence, the structure of **12** was elucidated to be methyl 2-chloro-6,10-dioxypyrido[2,1-*c*]-1,4-benzoxazine-8-carboxylate. This compound (**12**) may be an intermediate in the formation of the dimerized compound (**10**).

Chart 5

Fig. 1. The Molecular Structure of **9** Fig. 2. The Molecular Structure of **10**TABLE I. Positional ($\times 10^4$) and Thermal Parameters of **9** for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Cl(1)	3863 (2)	75 (1)	4882 (4)	6.9
O(1)	3483 (2)	2417 (2)	5555 (6)	2.0
O(2)	3531 (3)	4158 (2)	5319 (9)	3.9
O(3)	2788 (3)	3447 (2)	6046 (8)	3.1
O(4)	5519 (3)	3701 (2)	6235 (6)	2.5
O(5)	5399 (3)	4294 (2)	4182 (7)	2.9
O(6)	6228 (3)	3360 (2)	2061 (7)	3.2
O(7)	6051 (3)	2457 (2)	2004 (7)	2.5
N(1)	4790 (3)	1999 (2)	3738 (7)	4.8
C(1)	4327 (5)	1097 (3)	4314 (10)	4.0
C(2)	3777 (4)	763 (3)	5066 (10)	3.8
C(3)	3158 (5)	961 (3)	6023 (10)	4.2
C(4)	3070 (4)	1527 (3)	6158 (10)	3.8
C(5)	3613 (4)	1864 (2)	5347 (10)	3.0
C(6)	4239 (4)	1653 (3)	4501 (10)	3.1
C(7)	4690 (4)	2541 (3)	3893 (8)	2.6
C(8)	4019 (3)	2751 (2)	4857 (8)	2.4
C(9)	4007 (3)	3287 (2)	4852 (8)	2.4
C(10)	4710 (4)	3482 (3)	3851 (9)	3.1
C(11)	5106 (4)	2966 (3)	3326 (8)	2.8
C(12)	3437 (4)	3689 (3)	5426 (11)	4.0
C(13)	2177 (5)	3833 (4)	6550 (14)	6.4
C(14)	5257 (3)	3837 (2)	4927 (9)	2.7
C(15)	5939 (5)	4653 (3)	5057 (14)	5.6
C(16)	5840 (4)	2969 (3)	2395 (10)	3.5
C(17)	6790 (4)	2411 (4)	1088 (11)	4.7

Compound **3b** ($R_1 = R_2 = H$) was pyrolyzed in the same manner as in the case of **3b** ($R_1 = H$, $R_2 = Cl$), and two crystalline compounds were isolated from the reaction mixture. One (69.9% yield) was the deoxygenated cyclopentadieno-1,4-benzoxazine derivative (**13**) and the other was assigned to be the pyrido[2,1-*c*]-1,4-benzoxazine derivative (**14**). When **3b** ($R_1 = H$, $R_2 = Me$) was pyrolyzed in the same manner, **15** and **16** were obtained in 62.4% and 7.4%

TABLE II. Bond Lengths (Å) and Bond Angles (°) of **9** for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

Cl(1)–C(2)	1.723 (7)	O(1)–C(5)	1.402 (8)
O(2)–C(12)	1.180 (9)	O(3)–C(12)	1.355 (9)
O(4)–C(14)	1.190 (9)	O(5)–C(14)	1.307 (8)
O(6)–C(16)	1.207 (9)	N(1)–C(7)	1.363 (8)
N(1)–C(6)	1.414 (9)	C(2)–C(3)	1.396 (11)
C(1)–C(6)	1.397 (10)	C(5)–C(6)	1.371 (9)
C(1)–C(2)	1.392 (11)	C(8)–C(9)	1.332 (8)
C(3)–C(4)	1.418 (11)	C(9)–C(12)	1.468 (10)
C(4)–C(5)	1.409 (10)	O(5)–C(15)	1.462 (10)
C(7)–C(8)	1.478 (9)	C(11)–C(16)	1.459 (9)
C(9)–C(10)	1.524 (9)	O(1)–C(8)	1.356 (7)
C(10)–C(11)	1.509 (9)	O(7)–C(17)	1.465 (9)
C(7)–C(11)	1.352 (9)	O(3)–C(13)	1.473 (11)
C(10)–C(14)	1.548 (9)	O(7)–C(16)	1.359 (9)
C(5)–O(1)–C(8)	116.2 (5)	C(12)–O(3)–C(13)	113.2 (6)
C(14)–O(5)–C(15)	115.3 (6)	C(16)–O(7)–C(17)	114.6 (6)
C(6)–N(1)–C(7)	118.5 (5)	C(2)–C(1)–C(6)	118.0 (7)
Cl(1)–C(2)–C(1)	119.8 (6)	Cl(1)–C(2)–C(3)	117.5 (6)
C(1)–C(2)–C(3)	122.7 (6)	C(2)–C(3)–C(4)	118.2 (7)
C(3)–C(4)–C(5)	118.9 (7)	O(1)–C(5)–C(4)	115.0 (6)
O(1)–C(5)–C(6)	123.9 (6)	C(4)–C(5)–C(6)	121.1 (6)
N(1)–C(6)–C(1)	118.8 (6)	N(1)–C(6)–C(5)	120.2 (6)
C(1)–C(6)–C(5)	121.0 (6)	N(1)–C(7)–C(8)	119.6 (6)
N(1)–C(7)–C(11)	132.4 (6)	C(8)–C(7)–C(11)	108.0 (6)
O(1)–C(8)–C(7)	121.7 (5)	O(1)–C(8)–C(9)	126.9 (6)
C(7)–C(8)–C(9)	111.3 (5)	C(8)–C(9)–C(10)	107.8 (5)
C(8)–C(9)–C(12)	133.6 (6)	C(10)–C(9)–C(12)	118.2 (5)
C(9)–C(10)–C(11)	103.4 (5)	C(9)–C(10)–C(14)	111.2 (6)
C(7)–C(11)–C(10)	109.4 (6)	C(11)–C(10)–C(14)	111.7 (5)
C(10)–C(11)–C(16)	121.6 (6)	C(7)–C(11)–C(16)	129.0 (6)
O(2)–C(12)–C(9)	124.0 (7)	O(2)–C(12)–O(3)	125.1 (7)
O(4)–C(14)–O(5)	125.5 (6)	O(3)–C(12)–C(9)	110.9 (6)
O(5)–C(14)–C(10)	110.6 (6)	O(4)–C(14)–C(10)	123.8 (6)
O(6)–C(16)–C(11)	126.2 (7)	O(6)–C(16)–O(7)	123.8 (6)
O(7)–C(16)–C(11)	109.9 (6)		

yields, respectively. Similarly, **3b** ($R_1 = \text{Me}$, $R_2 = \text{H}$) gave **17** and **18** in 6.9% and 43.8% yields, respectively.

In conclusion, pyrido[1,2-*a*]quinoxalines and pyrido[1,2-*a*]pyrazines were easily synthesized by the pyrolysis of the methyl isocrotonate derivatives (**3a** and **6a**), respectively. It was found that the pyrolysis of **6b** afforded the expected pyrido-[2,1-*c*]-1,4-oxazine (**8b**) in a good yield, but the pyrolysis of **3b** containing an aromatic ring afforded somewhat different results. When the substituent was H or Me, the deoxygenated cyclopentadieno-1,4-benzoxazine derivatives (**13**, **15** or **17**) and pyrido[2,1-*c*]-1,4-benzoxazine derivatives (**14**, **16** or **18**) were formed, but when chlorine was substituted on the aromatic ring (**3b**, $R_1 = \text{H}$, $R_2 = \text{Cl}$), a complex mixture containing the dimerized product was obtained.

Experimental

All melting points were determined on a micro hot-stage apparatus (Mitamura, Tokyo) and are uncorrected. IR spectra (ν_{max}) in KBr disks were recorded on a Hitachi 215 infrared spectrophotometer and data are expressed in cm^{-1} . ^1H - and ^{13}C -NMR spectra were measured on a JNM-FX 100 spectrometer (JEOL, Tokyo) at 100 MHz and

TABLE III. Positional ($\times 10^4$) and Thermal Parameters of **10** for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Cl(1)	−2142 (2)	−1006 (1)	801 (2)	2.7
C(1)	−2110 (5)	−158 (4)	2794 (6)	2.1
C(2)	−3015 (5)	−715 (4)	4129 (6)	1.8
C(3)	−2922 (5)	−56 (4)	5718 (6)	2.3
C(4)	−1912 (5)	1122 (4)	5935 (5)	2.2
C(5)	−1001 (5)	1693 (4)	4602 (5)	1.6
C(6)	−1112 (5)	1048 (4)	2985 (5)	2.0
C(7)	−1169 (5)	2949 (4)	7934 (5)	2.2
C(8)	−424 (5)	3812 (4)	6431 (5)	2.0
C(9)	1053 (5)	3504 (4)	3747 (5)	1.6
C(10)	1697 (5)	5011 (4)	4142 (5)	1.5
C(11)	2105 (5)	5088 (4)	6045 (5)	1.8
C(12)	1076 (5)	4526 (4)	7175 (5)	1.9
C(13)	3563 (5)	5924 (4)	6577 (6)	1.9
C(14)	4932 (8)	6885 (7)	9030 (8)	2.2
O(1)	−1878 (4)	1674 (3)	7603 (4)	2.2
O(2)	−1201 (4)	3396 (3)	9362 (4)	2.8
O(3)	−4379 (4)	6576 (3)	5556 (4)	1.8
O(4)	3768 (4)	5878 (4)	8285 (4)	1.8
O(5)	1449 (4)	2891 (3)	2480 (4)	1.9
N(1)	−15 (4)	2924 (3)	4960 (4)	1.3

chemical shifts are expressed relative to 1% tetramethylsilane (TMS) as an internal standard; s=singlet, d=doublet, t=triplet, br=broad and m=multiplet. Low- and high-resolution MS were obtained with a GCMS-9000 spectrometer (Shimadzu, Tokyo) and JMS-DX 300 instrument (JEOL, Tokyo). Elemental analyses were done by the staff of the Analytical Center of the School of Pharmaceutical Sciences, Kitasato University (Tokyo), to whom our thanks are due. Thin-layer chromatography (TLC) was performed on Merck precoated Silica gel 60 F₂₅₄ plates. Preparative TLC was done with the same commercial product, 20 × 20 cm, with a thickness of 0.25, 0.5 or 2.0 mm. For column chromatography, silica gel (Wakogel C-200, Wako Pure Chemical Industries, Osaka) was used.

Photolysis was carried out in a flask with a 300 W high-pressure mercury lamp covered with a Pyrex filter under nitrogen atmosphere and cooled internally with running water. All the chemicals used were of reagent grade, and were used without further purification.

Compounds **2b**, **3b**, **5b** and **6b** have already been reported.²¹

According to the literature,⁴¹ **2a** and **5a** were easily prepared by the reaction of **1a** or **4a** with DMAD in MeOH at room temperature, respectively.

7-Chloro-3-methoxycarbonylmethylene-2-oxo-1,2,3,4-tetrahydroquinoxaline (2a, R₁ = Cl, R₂ = H)—Yellow needles, mp 246–248 °C (CH₂Cl₂–MeOH). Yield 83.2%. *Anal.* Calcd for C₁₁H₉N₂O₃: C, 52.29; H, 3.59; N, 11.09. Found: C, 52.23; H, 3.58; N, 11.03.

3-Methoxycarbonylmethylene-5-methyl-2-oxo-piperazine (5a, R₃ = R₄ = R₅ = H, R₆ = Me)—Pale yellow needles, mp 218–219.5 °C (CH₂Cl₂–MeOH). Yield 58.7%. *Anal.* Calcd for C₈H₁₂N₂O₃: C, 52.16; H, 6.57; N, 15.21. Found: C, 52.12; H, 6.60; N, 15.25. ¹³C-NMR (CDCl₃) δ: 18.66 (q), 45.61 (d), 46.68 (t), 50.73 (q), 86.45 (d), 148.28 (s), 161.05 (s), 170.89 (s).

3-Methoxycarbonylmethylene-2-oxo-decahydroquinoxaline (5a, R₃ = R₆ = H, R₄, R₅ = −(CH₂)₄−)—White prisms, mp 198–200 °C (CH₂Cl₂–MeOH). Yield 67.1%. ¹³C-NMR (CDCl₃) δ: 21.10 (t), 21.59 (t), 29.38 (t), 49.02 (d), 50.68 (d), 50.68 (q), 85.96 (d), 148.38 (s), 161.34 (s), 170.99 (s). *Anal.* Calcd for C₁₁H₁₆N₂O₃: C, 58.91; H, 7.19; N, 12.49. Found: C, 58.98; H, 7.28; N, 12.53.

Methyl 3-Oxo-1,2,3,4-tetrahydroquinoxaline-β,γ-bismethoxycarbonyl-Δ^{2,7}-isocrotonate (3a, R₁ = R₂ = H)—Method A (**3a** from **2a**): DMAD (5 ml) was added to a dry dioxane (30 ml) solution of **2a** (R₁ = R₂ = H, 3.0 g) and the mixture was refluxed overnight under a nitrogen atmosphere. The solvent was evaporated off *in vacuo* to afford a crystalline solid, which was washed with EtOH and recrystallized from CH₂Cl₂–EtOH to give 1.54 g of **3a** (mp 220–221 °C, yellow powder). The filtrate and washings were combined and the solvent was evaporated off *in vacuo*. The residue was chromatographed on silica gel with benzene–ether (9:1) as an eluent to give 1.25 g of **3a** (total 2.79 g, 56.4%).

Method B (**3a** from **1a**): DMAD (5 ml) was added to a dry dioxane (30 ml) solution of *o*-phenylenediamine (**1a**,

TABLE IV. Bond Lengths (Å) and Bond Angles (°) of **10** for Nonhydrogen Atoms with Their Standard Deviations in Parentheses

C(1)–Cl(1)	1.738 (4)	C(9)–C(10)	1.530 (5)
C(1)–C(2)	1.375 (6)	C(9)–N(1)	1.401 (5)
C(1)–C(6)	1.396 (6)	C(9)–O(5)	1.201 (5)
C(2)–C(3)	1.378 (6)	C(10)–C(12)	1.500 (5)
C(3)–C(4)	1.384 (6)	C(11)–C(12)	1.330 (6)
C(4)–C(5)	1.381 (5)	C(11)–C(13)	1.500 (6)
C(4)–O(1)	1.391 (5)	C(13)–O(3)	1.200 (5)
C(5)–C(6)	1.392 (5)	C(13)–O(4)	1.318 (5)
C(5)–N(1)	1.429 (5)	C(14)–O(4)	1.460 (7)
C(7)–C(8)	1.526 (5)	C(7)–O(1)	1.344 (5)
C(7)–O(2)	1.183 (5)	C(8)–C(12)	1.529 (6)
C(8)–N(1)	1.473 (5)	C(8)–C(10) ^{a)}	1.630 (6)
Cl(1)–C(1)–C(2)	119.5 (3)	N(1)–C(8)–C(10)	112.0 (3)
Cl(1)–C(1)–C(6)	117.9 (3)	C(10)–C(9)–N(1)	114.8 (3)
C(2)–C(1)–C(6)	122.6 (4)	C(10)–C(9)–O(5)	121.3 (3)
C(1)–C(2)–C(3)	118.4 (4)	N(1)–C(9)–O(5)	123.8 (3)
C(2)–C(3)–C(4)	119.6 (4)	C(9)–C(10)–C(11)	109.0 (3)
C(3)–C(4)–C(5)	122.5 (4)	C(9)–C(10)–C(8)	110.4 (3)
C(3)–C(4)–O(1)	114.7 (4)	C(11)–C(10)–C(8)	111.2 (3)
C(5)–C(4)–O(1)	122.8 (3)	C(10)–C(11)–C(12)	117.9 (4)
C(4)–C(5)–O(6)	118.1 (3)	C(10)–C(11)–C(13)	116.3 (3)
C(4)–C(5)–N(1)	118.0 (3)	C(12)–C(11)–C(13)	123.5 (4)
C(6)–C(5)–N(1)	123.9 (3)	C(8)–C(12)–C(11)	117.5 (3)
C(1)–C(6)–C(5)	118.7 (4)	C(4)–O(1)–C(7)	121.3 (3)
C(8)–C(7)–O(1)	118.9 (3)	C(5)–N(1)–C(8)	117.8 (3)
C(8)–C(7)–O(2)	121.9 (4)	C(5)–N(1)–C(9)	122.2 (3)
O(1)–C(7)–O(2)	119.1 (4)	C(8)–N(1)–C(9)	118.0 (3)
C(7)–C(8)–C(12)	106.3 (3)	C(11)–C(13)–O(3)	123.0 (4)
C(7)–C(8)–N(1)	113.1 (3)	C(11)–C(13)–O(4)	111.0 (3)
C(7)–C(8)–C(11)	105.3 (3)	O(3)–C(13)–O(4)	126.0 (4)
C(12)–C(8)–N(1)	108.8 (3)	C(13)–O(4)–C(14)	117.2 (4)
C(12)–C(8)–C(10)	111.3 (3)		

a) The bond length of C(8)–C(10) is longer than other C–C bond lengths, suggesting that this bond links the two components of the dimer.

1.08 g) and the mixture was refluxed overnight. After the same treatment as described above of the reaction mixture, 1.68 g (46.7%) of **3a** was obtained. ¹³C-NMR (DMSO-*d*₆) δ: 51.51 (q), 52.34 (q), 94.00 (s), 115.00 (d), 116.00 (d), 123.60 (s), 123.78 (d), 124.65 (d), 125.28 (d), 140.68 (s), 142.58 (s), 156.27 (s), 165.34 (s), 166.12 (s), 168.65 (s). *Anal.* Calcd for C₁₇H₁₆N₂O₇: C, 56.67; H, 4.47; N, 7.78. Found: C, 56.52; H, 4.37; N, 7.63.

Methyl 6-Chloro-3-oxo-1,2,3,4-tetrahydroquinoxaline-β,γ-bismethoxycarbonyl-Δ^{2,7}-isocrotonate (3a, R₁ = Cl, R₂ = H)—47.4% yield (Method A). Yellow powder, mp 195–197 °C (CH₂Cl₂–MeOH). ¹³C-NMR (CDCl₃) δ: 51.75 (q), 51.95 (q), 52.78 (q), 96.29 (s), 115.15 (d), 115.88 (d), 124.26 (d), 124.65 (s), 125.53 (d), 125.53 (s), 127.87 (s), 139.17 (s), 142.49 (s), 158.42 (s), 166.17 (s), 167.14 (s), 169.48 (s). *Anal.* Calcd for C₁₇H₁₅ClN₂O₇: C, 51.72; H, 3.83; N, 7.10. Found: C, 51.73; H, 3.82; N, 6.97.

Methyl 6-Methyl-3-oxo-piperazine-β,γ-bismethoxycarbonyl-Δ^{2,7}-isocrotonate (6a, R₃ = R₄ = R₅ = H, R₆ = Me)—53.1% yield (Method A). Yellow rods, mp 181–182.5 °C (EtOH). ¹³C-NMR (CDCl₃) δ: 17.98 (q), 45.81 (d), 46.73 (t), 51.26 (q), 51.41 (q), 52.29 (q), 124.75 (d), 144.00 (s), 144.80 (s), 145.70 (s), 161.29 (s), 166.02 (s), 167.24 (s), 169.29 (s). *Anal.* Calcd for C₁₄H₁₈N₂O₇: C, 51.53; H, 5.56; N, 8.59. Found: C, 51.39; H, 5.64; N, 8.55.

Methyl 3-Oxo-decahydroquinoxaline-β,γ-bismethoxycarbonyl-Δ^{2,7}-isocrotonate (6a, R₃ = R₆ = H, R₄, R₅ = –(CH₂)₄–)—47.7% yield (Method A). Yellow needles, mp 147–149 °C (ether). ¹³C-NMR (CDCl₃) δ: 21.34 (t), 28.56 (t), 29.29 (t), 49.22 (d), 49.95 (d), 51.17 (q), 51.41 (q), 52.24 (q), 94.00 (s), 124.26 (d), 143.21 (s), 146.19 (s), 161.93 (s), 166.12 (s), 167.24 (s), 169.43 (s). *Anal.* Calcd for C₁₇H₂₂N₂O₇: C, 55.73; H, 6.05; N, 7.65. Found: C, 55.90; H, 6.03; N, 7.58.

General Procedure for the Thermal Reaction of 3 and 6—A solution of **3** or **6** (0.082 mol) in dry DMSO (70 ml) was refluxed for 30 min or 1 h under a nitrogen atmosphere. After removal of the solvent *in vacuo* on a hot bath,

TABLE V. Spectral Data for Compounds **2**, **3** and **5–18**

Compd. No.	MS m/z (M^+)	IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1}	$^1\text{H-NMR}$ (CDCl_3) ^{a)} δ
2a ($R_1 = R_2 = \text{H}$)	218	1690, 1620	^{a)} 3.73 (3H, s), 5.57 (1H, s), 7.02–7.60 (4H, m), 9.05 (1H, br), 11.13 (1H, br)
2a ($R_1 = \text{Cl}$, $R_2 = \text{H}$)	252, 254	1680, 1620	^{a)} 3.82 (3H, s), 5.52 (1H, s), 7.03–7.53 (3H, m), 11.00 (1H, br)
3a ($R_1 = R_2 = \text{H}$)	360	1720, 1650, 1595	3.68, 3.71, 3.76 (each 3H, s), 6.90 (1H, s), 7.00–7.60 (4H, m), 10.57 (1H, br), 12.23 (1H, br)
3a ($R_1 = \text{Cl}$, $R_2 = \text{H}$)	394, 396	1690, 1620	3.72 (6H, s), 3.84 (3H, s), 6.92 (1H, s), 6.90–7.08 (3H, m), 11.22 (1H, br), 12.15 (1H, br)
5a ($R_6 = \text{Me}$)	184	1680, 1620	1.28 (3H, d, $J = 6.2$ Hz), 3.00–3.60 (2H, m), 3.69 (3H, s), 3.69–4.00 (1H, m), 5.61 (1H, s), 7.23 (1H, br), 8.27 (1H, br)
5a ($R_4, R_5 = -(\text{CH}_2)_4-$)	222	1680, 1645, 1610	1.00–1.95 (8H, br), 3.40–3.75 (2H, br), 3.69 (3H, s), 5.60 (1H, s), 7.50 (1H, br), 8.20 (1H, br)
6a ($R_6 = \text{Me}$)	326	1710, 1640, 1610	1.24 (3H, d, $J = 6.2$ Hz), 3.00–4.00 (3H, br), 3.61, 3.67, 3.74 (each 3H, s), 6.74 (1H, s), 7.24 (1H, br), 9.30 (1H, br)
6a ($R_4, R_5 = -(\text{CH}_2)_4-$)	366	1710, 1640, 1575	1.00–1.95 (8H, br), 3.60–3.70 (2H, br), 3.60, 3.66, 3.70 (each 3H, s), 6.70 (1H, s), 8.22 (1H, br), 9.29 (1H, br)
7 ($R_1 = R_2 = \text{H}$)	328	1740, 1710, 1650, 1580	^{a)} 3.76, 3.85 (each 3H, s), 7.00–7.30 (3H, m), 7.27 (1H, s), 9.11 (1H, d, $J = 9.0$ Hz), 12.02 (1H, br)
7 ($R_1 = \text{Cl}$, $R_2 = \text{H}$)	362, 364	1725, 1660, 1590	^{a)} 3.76, 3.84 (each 3H, s), 7.20–7.30 (3H, m), 7.28 (1H, s), 9.16 (1H, d, $J = 9.0$ Hz), 12.09 (1H, br)
8a ($R_6 = \text{Me}$)	294	1740, 1660	1.40 (3H, d, $J = 6.2$ Hz), 3.33–3.90 (2H, m), 3.88, 3.90 (each 3H, s), 4.69 (1H, m), 7.35 (1H, s), 8.14 (1H, br)
8a ($R_4, R_5 = -(\text{CH}_2)_4-$)	334	1740, 1700, 1660	1.30–2.30 (8H, br), 3.87, 3.90 (each 3H, s), 3.90 (1H, br), 4.90 (1H, br), 7.32 (1H, s), 8.55 (1H, br)
8b ($R_5 = R_6 = \text{Me}$)	309	1730, 1665, 1610	1.72 (6H, s), 3.91 (6H, s), 4.27 (2H, s), 7.27 (1H, s)
9	379, 381	1710, 1690, 1660, 1620	^{a)} 3.60, 3.68, 3.70 (each 3H, s), 4.47 (1H, s), 7.50 (1H, d, $J = 2.4$ Hz), 7.11 (1H, d, $J = 8.6$ Hz), 6.95 (1H, dd, $J = 8.6, 2.4$ Hz)
11	363, 365	1760, 1740, 1685	3.95, 4.00 (each 3H, s), 7.24 (1H, d, $J = 8.8$ Hz), 7.41 (1H, dd, $J = 8.8, 2.2$ Hz), 9.29 (1H, d, $J = 2.2$ Hz)
12	305, 307	1750, 1675, 1620	4.00 (3H, s), 7.25 (1H, d, $J = 8.1$ Hz), 7.40 (1H, dd, $J = 8.1, 2.4$ Hz), 7.59 (1H, d, $J = 2.0$ Hz), 8.01 (1H, d, $J = 2.0$ Hz), 9.51 (1H, d, $J = 2.4$ Hz)
13	345	1720, 1700, 1640	3.75, 3.79, 3.83 (each 3H, s), 4.60 (1H, s), 6.80–7.20 (4H, m), 8.45 (1H, br)
14	329	1760, 1730, 1675, 1590	3.95, 3.99 (each 3H, s), 7.27–7.38 (3H, m), 7.58 (1H, s), 9.15 (1H, br)
15	359	1700, 1660, 1620	2.28 (3H, s), 3.75, 3.77, 3.81 (each 3H, s), 4.57 (1H, s), 6.64 (1H, br), 6.82 (1H, d, $J = 8.1$ Hz), 7.09 (1H, d, $J = 8.1$ Hz), 8.35 (1H, br)
16	343	1730, 1680	2.42 (3H, s), 3.95, 4.00 (each 3H, s), 7.19–7.26 (2H, br), 7.60 (1H, s), 8.99 (1H, br)
17	359	1700, 1655, 1615	2.29 (3H, s), 3.74, 3.78, 3.82 (each 3H, s), 4.62 (1H, s), 6.73 (1H, d, $J = 10.0$ Hz), 6.88 (1H, d, $J = 10.0$ Hz), 7.03 (1H, br), 8.35 (1H, br)
18	343	1755, 1730, 1670	2.42 (3H, s), 3.95, 4.00 (each 3H, s), 7.00–7.26 (2H, br), 7.60 (1H, s), 9.08 (1H, d, $J = 9.3$ Hz)

a) DMSO- d_6 .

extraction of the reaction product with ethyl acetate or methylene chloride followed by evaporation of the solvent *in vacuo* afforded a brownish crystalline solid or oil which was purified by column chromatography and/or preparative TLC, and finally by recrystallization from an appropriate solvent.

Dimethyl 5,6-Dihydro-6,10-dioxo-10H-pyrido[1,2-a]quinoxaline-7,8-dicarboxylate (7, $R_1 = R_2 = H$)—According to the general procedure, the crude product was obtained from **3a** ($R_1 = R_2 = H$, 3.0 g) and recrystallized from CH_2Cl_2 -MeOH to afford yellow needles, mp 282–284 °C. Yield 1.75 g (63.9%). ^{13}C -NMR (DMSO- d_6) δ : 52.14 (q), 53.12 (q), 95.46 (s), 116.03 (d), 120.90 (d), 122.26 (d), 122.85 (s), 125.77 (d), 128.11 (d), 128.31 (s), 133.42 (s), 136.78 (s), 154.43 (s), 160.51 (s), 163.34 (s), 165.49 (s). *Anal.* Calcd for $C_{16}H_{12}N_2O_6$: C, 58.54; H, 3.68; N, 8.53. Found: C, 58.52; H, 3.51; N, 8.29.

Photolysis of 3a—A solution of **3a** ($R_1 = R_2 = H$, 0.3 g) in dry MeOH (400 ml) was irradiated for 6 h. The crystalline solid obtained upon removal of the solvent was washed with MeOH to give 0.086 g of **7**. The filtrate and washings were combined and the solvent was evaporated off *in vacuo* and purified by preparative TLC to give a further 0.025 g of **7** (total 0.111 g, 40.5%).

Dimethyl 3-Chloro-5,6-dihydro-6,10-dioxo-10H-pyrido[1,2-a]quinoxaline-7,8-dicarboxylate (7, $R_1 = Cl$, $R_2 = H$)—According to the general procedure, the crude product was obtained from **3a** ($R_1 = Cl$, $R_2 = H$, 1.0 g) and recrystallized from CH_2Cl_2 -MeOH to afford a brownish powder, mp 295–296 °C. Yield 0.511 g (51.7%). *Anal.* Calcd for $C_{16}H_{11}ClN_2O_6$: C, 52.97; H, 3.06; N, 7.72. Found: C, 52.76; H, 2.89; N, 7.60.

Dimethyl 4-Methyl-1,6-dioxo-1,2,3,4-tetrahydro-6H-pyrido[1,2-a]pyrazine-8,9-dicarboxylate (8a, $R_3 = R_4 = R_5 = H$, $R_6 = Me$)—According to the general procedure, the crude product was obtained from **6a** ($R_3 = R_4 = R_5 = H$, $R_6 = Me$, 0.24 g) and recrystallized from CH_2Cl_2 -ether to afford pale yellow cubes, mp 202.5–203.5 °C. Yield 0.173 g (79.7%). ^{13}C -NMR ($CDCl_3$) δ : 18.03 (q), 44.78 (d), 46.34 (t), 52.92 (q), 53.31 (q), 115.73 (s), 126.31 (d), 134.64 (s), 138.29 (s), 158.86 (s), 159.73 (s), 163.39 (s), 166.27 (s). *Anal.* Calcd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.52. Found: C, 52.92; H, 4.81; N, 9.31.

Dimethyl 6,10-Dioxo-10H-pyrido[1,2-a]decahydroquinoxaline-7,8-dicarboxylate (8a, $R_3 = R_6 = H$, $R_4, R_5 = -(CH_2)_4-$)—According to the general procedure, the crude product was obtained from **6a** ($R_3 = R_6 = H$, $R_4, R_5 = -(CH_2)_4-$, 1.0 g) and recrystallized from MeOH to afford pale yellow prisms, mp 243–245 °C. Yield 0.597 g (65.4%). ^{13}C -NMR ($CDCl_3$) δ : 18.57 (t), 23.73 (t), 25.14 (t), 28.65 (t), 47.61 (d), 51.70 (d), 52.68 (q), 53.26 (q), 115.88 (s), 126.36 (d), 133.96 (s), 138.05 (s), 159.20 (s), 159.78 (s), 163.44 (s), 166.32 (s). *Anal.* Calcd for $C_{16}H_{18}N_2O_6$: C, 57.48; H, 5.43; N, 8.38. Found: C, 57.35; H, 5.35; N, 8.30.

Dimethyl 3,4-Dihydro-4,4-dimethylpyrido[2,1-c]-1,4-oxazine-1,6-dioxo-8,9-dicarboxylate (8b, $R_3 = R_4 = H$, $R_5 = R_6 = Me$)—According to the general procedure, the crude product was obtained from **6b** ($R_3 = R_4 = H$, $R_5 = R_6 = Me$, 0.5 g) and recrystallized from MeOH-ether to afford white rods, mp 203–205 °C. Yield 0.317 g (69.9%). *Anal.* Calcd for $C_{14}H_{15}NO_7$: C, 54.37; H, 4.89; N, 4.53. Found: C, 54.36; H, 4.86; N, 4.54.

Thermal Reaction of 3b ($R_1 = H$, $R_2 = Cl$)—1) A solution of **3b** ($R_1 = H$, $R_2 = Cl$, 3.0 g) in DMSO (30 ml) was refluxed for 1 h under a nitrogen atmosphere. According to the general procedure, the residue was subjected to silica gel column chromatography (30 g) to give **9** (eluted with 3% ether in benzene), which was recrystallized from CH_2Cl_2 -MeOH to afford needles, mp 239–241 °C. Yield 1.17 g (38.8%). ^{13}C -NMR (DMSO- d_6) δ : 49.61 (d), 51.02 (q), 51.51 (q), 52.14 (q), 98.53 (s), 107.64 (s), 116.22 (d), 117.93 (d), 122.19 (d), 126.45 (s), 128.45 (s), 138.88 (s), 141.65 (s), 152.87 (s), 161.59 (s), 163.34 (s), 169.58 (s). *Anal.* Calcd for $C_{17}H_{14}ClNO_7$: C, 53.75; H, 3.69; N, 3.69. Found: C, 53.49; H, 3.71; N, 3.73. **10** (0.159 g, 3.4%) was isolated by preparative TLC (benzene: ethyl acetate = 9:1) of the second fraction (eluted with 5% ether in benzene) of the above column chromatography. This compound (**10**) was repeatedly recrystallized from CH_2Cl_2 -ether to give pure colorless prisms (mp 178 °C).

2) A solution of **3b** ($R_1 = H$, $R_2 = Cl$, 3.0 g) in dry DMSO (30 ml) was refluxed for 30 min under a nitrogen atmosphere. According to the general procedure, the residue was subjected to silica gel column chromatography (30 g) to give **12** (eluted with 1% ether in benzene), which was recrystallized from CH_2Cl_2 -ether to afford yellow needles, mp 176–178 °C. Yield 0.095 g (4.1%). ^{13}C -NMR ($CDCl_3$) δ : 53.41 (q), 111.98 (d), 118.56 (d), 121.39 (d), 123.09 (s), 128.79 (d), 128.98 (s), 130.26 (d), 130.69 (s), 138.29 (s), 139.95 (s), 154.13 (s), 161.01 (s), 163.20 (s). *Anal.* Calcd for $C_{14}H_8ClNO_5$: C, 54.96; H, 2.64; N, 4.58. Found: C, 54.54; H, 2.59; N, 4.50. The high-resolution MS showed m/z 305.00895 (Calcd 305.00903). **11**, eluted with 1.5% ether in benzene, was recrystallized from CH_2Cl_2 -ether to afford pale yellow needles, mp 203–204 °C. Yield 0.429 g (11.9%). ^{13}C -NMR ($CDCl_3$) δ : 53.46 (q), 53.65 (q), 118.42 (d), 120.07 (s), 121.24 (d), 122.51 (s), 126.84 (s), 129.13 (d), 130.64 (s), 130.79 (d), 136.93 (s), 139.81 (s), 153.01 (s), 159.64 (s), 162.32 (s), 164.90 (s). *Anal.* Calcd for $C_{16}H_{10}ClNO_7$: C, 52.83; H, 2.78; N, 3.85. Found: C, 52.87; H, 2.70; N, 4.20. The high-resolution MS showed m/z 365.00971 (Calcd 365.01154).

X-Ray Analysis—1) The crystals of **9** are orthorhombic [$a = 17.082$ (3) Å, $b = 24.832$ (9) Å, $c = 8.028$ (2) Å, $V = 3405$ Å³, $Z = 8$, $D_{calc.} = 1.482$ g cm⁻³, space group P_{bca}]. The reflection data were collected on a Rigaku four-circle diffractometer using graphite-monochromated Cu-K α radiation. Those reflections having an intensity exceeding 3 times the corresponding standard deviations were collected, and 2053 reflections out of 2375 reflections were used as data. The structure was solved by the heavy-atom (chlorine) method and refined by the block-diagonal least-squares method to a final R value of 0.099.

2) The crystals of **10** are monoclinic [$a = 8.5490$ Å, $b = 9.3740$ Å, $c = 7.6670$ Å, $V = 613.61$ Å³, $Z = 1$, $D_{calc.} =$

1.654 g cm⁻¹, space group $P\bar{1}$]. The reflection data were collected on a Rigaku four-circle diffractometer using graphite-monochromated Cu-K α radiation. Those reflections having an intensity exceeding 3 times the corresponding standard deviations were collected and 1724 reflections out of 1984 reflections were used as data. The structure was solved by the heavy-atom (chlorine) method and refined by the block-diagonal least-squares method to a final *R* value of 0.074.

Thermal Reaction of 3b ($R_1 = R_2 = H$)—A solution of **3b** ($R_1 = R_2 = H$, 3.0 g) in dry DMSO (30 ml) was refluxed for 30 min under a nitrogen atmosphere. According to the general procedure, the residue was purified by silica gel column chromatography (70 g) with benzene–ether as an eluent to give **14** (2% ether–benzene), which was recrystallized from CH₂Cl₂–ether to afford pale yellow needles, mp 205–206 °C. Yield 0.166 g (6.1%). ¹³C-NMR (CDCl₃) δ : 53.41 (q), 53.55 (q), 117.44 (d), 121.19 (d), 121.97 (s), 125.33 (d), 129.13 (d), 129.13 (s), 130.69 (d), 136.69 (s), 141.17 (s), 153.54 (s), 159.78 (s), 162.46 (s), 165.19 (s). *Anal.* Calcd for C₁₄H₁₁NO₇: C, 58.36; H, 3.37; N, 4.25. Found: C, 58.13; H, 3.29; N, 4.27. Compound **13**, eluted with 3% ether–benzene, was recrystallized from CH₂Cl₂–MeOH to afford pale yellow needles, mp 235–238 °C. Yield 1.955 g (68.2%). ¹³C-NMR (CDCl₃) δ : 49.90 (d), 51.36 (q), 51.70 (q), 52.58 (q), 97.85 (s), 108.18 (s), 115.49 (d), 117.54 (d), 123.24 (d), 124.21 (s), 125.04 (d), 140.93 (s), 144.09 (s), 153.50 (s), 162.51 (s), 165.24 (s), 170.31 (s). *Anal.* Calcd for C₁₇H₁₅NO₇: C, 59.13; H, 4.38; N, 4.06. Found: C, 59.06; H, 4.38; N, 3.98.

Thermal Reaction of 3b ($R_1 = H$, $R_2 = Me$)—A solution of **3b** ($R_1 = H$, $R_2 = Me$, 4.0 g) in dry DMSO (40 ml) was refluxed for 1 h under a nitrogen atmosphere. According to the general procedure, the residue was purified by silica gel column chromatography (70 g) with benzene–ether as an eluent to give **16** (1% ether–benzene), which was recrystallized from ethyl acetate to afford yellow needles, mp 201–202 °C. Yield 0.272 g (7.4%). ¹³C-NMR (CDCl₃) δ : 21.44 (q), 53.41 (q), 53.55 (q), 117.05 (d), 119.68 (s), 121.14 (d), 121.63 (s), 127.43 (s), 129.76 (d), 130.54 (d), 135.42 (s), 136.64 (s), 139.12 (s), 153.69 (s), 159.84 (s), 162.57 (s), 165.24 (s). *Anal.* Calcd for C₁₇H₁₃NO₇: C, 59.48; H, 3.82; N, 4.08. Found: C, 59.02; H, 3.76; N, 3.96. The high-resolution MS showed *m/z* 343.06813 (Calcd 343.06910). Compound **15**, eluted with 1.5% ether–benzene, was recrystallized from CH₂Cl₂–MeOH to afford yellow plates, mp 247–249 °C. Yield 2.39 g (62.4%). *Anal.* Calcd for C₁₈H₁₇NO₇: C, 60.16; H, 4.79; N, 3.90. Found: C, 60.03; H, 4.73; N, 3.90.

Thermal Reaction of 3b ($R_1 = Me$, $R_2 = H$)—A solution of **3b** ($R_1 = Me$, $R_2 = H$, 1.79 g) in dry DMSO (60 ml) was refluxed for 30 min under a nitrogen atmosphere. According to the general procedure, the residue was purified by silica gel column chromatography (40 g) with benzene–ether as an eluent to give **18** (1% ether–benzene), which was recrystallized from CH₂Cl₂–ether to afford pale yellow plates, mp 251–253 °C. Yield 0.717 g (43.8%). *Anal.* Calcd for C₁₇H₁₃NO₇: C, 59.48; H, 3.82; N, 4.08. Found: C, 59.42; H, 3.74; N, 4.00. Compound **17**, eluted with 1.5% ether–benzene, was recrystallized from CH₂Cl₂–ether to afford pale yellow needles, mp 269–270 °C. Yield 0.118 g (6.9%). *Anal.* Calcd for C₁₈H₁₇NO₇: C, 60.16; H, 4.77; N, 3.90. Found: C, 60.26; H, 4.59; N, 3.30. The high-resolution MS showed *m/z* 359.10079 (Calcd 359.10038).

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- 6) In the previous paper,²⁾ we termed **3** and **6**, trimethyl aconitate derivatives.